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To cite this version:

J.P. Bachheimer. The stripe phase of the $\beta$-INC-$\alpha$ transformation of quartz under a uniaxial stress: optical and dilatometric investigation. Journal de Physique, 1988, 49 (3), pp.457-462. <10.1051/jphys:01988004903045700>. <jpa-00210716>

HAL Id: jpa-00210716
https://hal.archives-ouvertes.fr/jpa-00210716
Submitted on 1 Jan 1988

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The stripe phase of the $\beta$-INC-$\alpha$ transformation of quartz under a uniaxial stress: optical and dilatometric investigation

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(Réçu le 17 septembre 1987, accepté le 4 novembre 1987)

Résumé. — Un cristal de quartz soumis à une contrainte uniaxiale $\sigma_{yy}$ montre l'existence d'anomalies entre les phases $\beta$ et incommensurable ($3q$) sur : la rotation et la dépolarisation de la lumière, la biréfringence et la dilatation. Ces anomalies révèlent l'existence de la phase monomodulée ($1q$) récemment prévue théoriquement et découverte sous contrainte $\sigma_{yy}$ par diffraction des neutrons. Elles permettent d'en préciser le diagramme de phase et de donner aussi celui-ci pour le cas $\sigma_{xx}$. Ces diagrammes révèlent que la phase $1q$ existe aussi à contrainte nulle sur un intervalle de quelques centièmes de K en température. En accord avec les prévisions théoriques cet intervalle varie plus vite avec $\sigma_{yy}$ qu'avec $\sigma_{xx}$ et la transition $1q \leftrightarrow 3q$ est du 1er ordre.

Abstract. — Anomalies of optical rotation, light depolarization, birefringence and dilatation of crystal quartz under $\sigma_{yy}$ uniaxial stresses confirm the existence of an incommensurate ($1q$) stripe phase, recently expected theoretically and discovered by neutron scattering, between the $\beta$ and the INC ($3q$) phases. The phase diagram is determined to a better resolution than with neutron diffraction. These anomalies allow us to obtain also the phase diagram of the $1q$ phase under $\sigma_{xx}$ stresses. Both phase diagrams show the presence of the $1q$ phase over a small temperature range (a few hundredth K), even at zero stress. As expected from theory, the variation of its temperature interval is found to be larger with $\sigma_{yy}$ stress than with $\sigma_{xx}$ stress and the $1q \leftrightarrow 3q$ transition appears to be first-order.

1. Introduction.

The study of the effect of stresses on phase transitions in solids is of both theoretical and practical interest. In quartz, stresses cause the shift (10 K/kbar for $\sigma_{xx}$ or $\sigma_{yy}$ [1]) of the $\alpha$-$\beta$ ($\sim 573^\circ$ C) transition which influences all the properties down to ambient temperature because the order parameter has not reached saturation [2]. Among other stress effects we may mention twinning [3] or detwinning [4], change of the morphology of the interface between the high and the low-temperature phases [5] and (the latest discovered [8]) induction of a new $1q$ INC phase between the $\beta$ and the ($3q$) incommensurate phases. This new phase is the subject of this paper. Let us recall that the $\beta$ and the $\alpha$ phase are separated by an incommensurate (INC-$3q$) phase which exists in a temperature range of about 1.3 K on cooling [6, 7]. In appearance it resembles [10] a fine network of triangular columns (cross-section $\sim 100 \text{ Å}$) parallel to the $Z$ axis and it is explained [11] by the phenomenological Landau theory as the result of the superposition of 3 modulation waves $120^\circ$ apart (Fig. 1a). When one adds to this theory [8] the effect of a uniaxial stress ($\sigma_{yy}$ or $\sigma_{xx}$) — which breaks the symmetry of order 6 — a « $1q$ » phase between the $\beta$ and the INC ($3q$) phases is expected. According to the sign of $(\sigma_{xx} - \sigma_{yy})$ the wave vector of the $1q$ (INC) phase corresponds to one of the directions of the $3q$ (INC) wave vectors (Fig. 1c-d). This has been verified recently by neutron scattering but only with $\sigma_{yy}$ stress [8] (Fig. 1c).

In this paper we first of all give the result obtained from optical investigations with $\sigma_{yy}$ stress which allows us to determine the $\sigma_{yy}$ phase diagram obtained with neutron diffraction. Secondly we investigate the $\sigma_{xx}$ phase diagram to compare the
Previously evoked theory predicting a temperature range of the $1q$ phase smaller than with $\sigma_{yy}$ stress. Experimental investigations involve rotatory power, optical polarization, birefringence and dilatation measurements. In a preceding paper we have already shown that the $\beta$-INC transition is marked by a change of slope in dilatation and birefringence curves [6]. It is still more evident in rotatory power variation where it is also accompanied by a small peak of light depolarization [12].

The same techniques have been used in the present case to determine the stress dependence of these properties.

2. Apparatus.

The measurements were made on parallelepipeds ($7.5 \times 7.5 \times 30 \text{ mm}^3$) of natural colourless and of good optical quality single quartz crystal with polished faces perpendicular to the crystallographic axis. The thermal apparatus has already been briefly described [1, 12]; it allows measurements of dilatation ($\Delta L$) with uniaxial compressive stress (by means of lever and weights) to be taken along the 30 mm height of the sample. A resistance thermometer bridge gives a temperature resolution better than 0.006 K. Two laser beams ($\lambda = 6328 \text{ Å}$) are allowed to pass half way up and through the sample by mean of four holes of $\sim 1.5 \text{ mm}$ diameter. Optical rotation ($\Delta R = \rho \cdot d$ $d = 7.5 \text{ mm}$) and light polarization ($I_\perp$) are measured along the $Z$ axis using the method previously described [12] (the exit face of the sample is cut at an angle of $\sim 18^\circ$ with respect to the entry face in order to reduce interference effects). The values of the phase birefringence $\varphi = \pi \Delta n \lambda$ ($\Delta n =$ birefringence, $\lambda = 7.5 \text{ mm}$) were measured in a direction perpendicular to the $Z$ axis (at a small angle of about $3^\circ$ to avoid interference effects) by the de Senarmont method using an automatic device. $\Delta L$, $\Delta R$, $I_\perp$ and $\Delta \varphi$ are continuously recorded on $X$ - $Y_1$ - $Y_2$ recorders with the temperature on the $X$ axis.

Stress homogeneity was checked at room temperature from birefringence (photo-elastic effect) point-by-point exploration of the whole sample. On the horizontal (lasers) plane we find an inhomogeneity of about 3% increasing to approximately 10% under the stainless steel piston which supplies the pressure (contact with a gold foil 0.1 mm thick). This residual inhomogeneity (very sensitive to the centering of the sample) appears to be intrinsic both from the geometric form of the sample and boundary conditions of stress application. At ambient temperature, we also discovered that the best extinctions on both directions are obtained under the best homogeneity stress conditions. These best values of extinction are taken as references to judge the quality of stress homogeneity at higher temperatures.

It was thus necessary, in order to maintain stress evenness, to add two small jacks acting on the low piston to counter balance the deformation induced in the apparatus by large temperature or stress variations.

3. Results.

We will first present the results obtained with $\sigma_{yy}$ stresses and then with $\sigma_{xx}$ stresses. All curves are obtained with a typical temperature drift $\sim 0.03 \text{ K/min}$ and for discrete values of the stress (our apparatus does not allow us to pass continuously from $\sigma = 0$ to $\sigma \neq 0$).

3.1 $\sigma_{yy}$ STRESSES. — Figure 2a illustrates some selected examples of the evolution under stress of the dilatation in the $\beta$-INC region which is defined on the main ($\alpha$-INC) hysteresis cycle shown (dotted lines) at small stress (10 bars) with a vertical reduction of four. For small stresses we see the usual change of slope previously [6] identified as the $\beta \leftrightarrow$ INC transition. While $\sigma_{yy}$ increases a second change of slope appears which delimits a region of increasing temperature width with a nearly constant expansion coefficient. The birefringence variation (Fig. 2b) looks like the dilatation variation (they are generally proportional in quartz [13]) but with more details: a remarkable linearity between $T_{i1}$ and $T_{i3}$ as a function of the temperature ($\frac{d\varphi}{dT}$ decreases from $38^\circ$K at zero stress to $26^\circ$K at 700 bars) and, in addition, evidence of a small «vertical» discontinuity at $T_{i3}$. This is more apparent at medium stress (291 bars) as shown on a large scale in figure 3b where one can also distinguish another small «vertical» discontinuity at $T_{i1}$ which however disappears at higher stresses. In figure 3b we have also plotted (dotted line) the birefringence variation recorded at zero stress (with adequate $\Delta T$ and $\Delta \varphi$ shifts). The two curves can be superimposed except in the linear region where they intersect. This conclusion applies to all studied $\sigma_{yy}$ stresses.

Rotatory power ($AR$) and light depolarization ($I_\perp$) are shown on the left of figure 2c-c' with small
Fig. 2. — The temperature (cooling) dependance (in the β-INC region) of the dilatation $\Delta L$ (a) the birefringence $\Delta \varphi$ (b) the rotation $\Delta R$ (c) and the depolarization $\Delta I_\perp$ (c') of the light propagating along the Z axis for some values of $\sigma_{yy}$ (bars). The main (α-INC) hysteresis cycle is shown (a) (dotted lines) with a vertical reduction of four. (10 bars) stress: β-INC transition is marked by an angular point on $\Delta R$ and the appearance of two small peaks on $I_\perp$.

At higher stress the rotatory power effect is superimposed on photoelastic induced birefringence. The emergent beam is generally elliptically polarized [14] — following an oscillating function of the stress (*) — so that our extinction method of detecting variation of rotatory power gives us in fact the rotation ($\Delta R$) of the ellipse while the residual light ($I_\perp$) after the analyser gives the ellipticity.

To preserve the sensitivity of the automatic apparatus it is sometimes better to interpose a $\lambda/4$ plate (the effect of which is to interchange $\Delta R$ and $\Delta I_\perp$) in order to reduce the value of $I_\perp$. This operation is carried out only once in the β phase, without readjustment during temperature scans. Because we are interested only in the anomalies of the $\Delta R$ and $\Delta I_\perp$ curves the presence of the $\lambda/4$ plate is not subsequently shown.

Figure 2c-c' shows some aspects of the two anomalies which appear at $T_{i1}$ and $T_{i3}$ under $\sigma_{yy}$ stress (sometimes one of those anomalies is difficult to distinguish on one of these curves but both curves always allow $T_{i1}$ and $T_{i3}$ to be defined. Figure 3c-c' shows that the peaks correspond to the vertical discontinuities, on the birefringence curves (Fig. 3b). As shown in figure 4a-a' these peaks are particularly useful to determine $T_{i1}$ and $T_{i3}$ at low stress at which the anomalies on the birefringence curves are weak (Fig. 4b). We also observe that the peaks remain visible (although broadening) in spite of an inhomogeneous stress distribution (induced by the jack or by bad setting) while the anomalies on the birefringence and dilatation curves are smoothed out. The dotted lines in figure 4 show, for example at 52 bars, a heating curve obtained after cooling within the INC (3 q) phase. We note a hysteresis of 0.012 K at $T_{i3}$ (which increases to 0.03 K at 700 bars) while there is no hysteresis at $T_{i1}$. (Sometimes a very small hysteresis (0.006 K) appears at $T_{i1}$ and only for medium stress). We also note hysteresis (0.02 K) during the INC (3 q) phase.

(*) Starting, for instance, from formulae given in [15], the ellipticity $\chi$ of the transmitted light is $\sin 2 \chi = \sin \left[ 2 \arctg \left( \frac{\rho d}{\alpha \sigma} \right) \right] \sin^2 \sqrt{(\alpha \sigma)^2 + (\rho d)^2}$ with $(\alpha \sigma)$ is the induced phase angle birefringence, $\alpha$ a photoelastic coefficient. In our experiment we find $\chi = 0$ for $\alpha = 0$ ; 126 ; 512 bars.
The evolution under low $\sigma_{yy}$ stresses (5, 10, ... bars) of the anomalies which mark the 1$q$ phase. Optical rotation $\Delta \rho$ (a), light depolarization $\Delta I_{\perp}$ (a'), birefringence $\Delta \varphi$ (b) obtained in cooling — dot line: example with heating (after cooling in the INC (3$q$) phase).

which is known to be due to pinning of the incommensurate modulation by defects [16].

The change of slope on the dilatation and birefringence curves together with the anomalies in light polarisation and rotation are signs of the presence of a supplementary phase between the $\beta$ and INC (3$q$) phases. To compare our results with neutron scattering results [8] under $\sigma_{yy}$ stress, we have plotted a phase diagram with $T_{I1}$ and $T_{I3}$ temperatures (*) (Fig. 5) together with points determined by neutron diffraction: the agreement in the results leads us to conclude that $T_{I1}$ and $T_{I3}$ are the limits of the 1$q$ phase. The optical measurements are however more accurate and enable us to deduce unambiguously that this 1$q$ phase also exists at zero stress over a temperature range of about 0.07 K.

3.2 $\sigma_{xx}$ STRESSES. — In this case we also clearly found an intermediate stress-induced phase, as the preceding effects described with $\sigma_{yy}$ are also observed. However the $T_{I1} - T_{I3}$ temperature difference is smaller, and we therefore had greater difficulty to observe it, especially by birefringence and dilatation studies. Figure 6 shows the variation of $\Delta R$, $\Delta I_{\perp}$, $\Delta \varphi$ and $\Delta L$ at medium (316 bars) stress (to compare with Fig. 3 note that the temperature scale is expanded by a factor of two). On the birefringence curve it is also possible to note a small inflexion (which disappears at low and high stress) at $T_{I3}$, reminiscent of the similar discontinuity under $\sigma_{yy}$. In general we find the same temperature hysteresis at $T_{I1}$ and $T_{I3}$ with variable values (~0.02 ± 0.02 K) as a function of stress, depending also on the depth of the excursion into the 3$q$ phase. In figure 7 we plot the stress dependence of $T_{I1}$ and $T_{I3}$ which gives us (following the conclusion from $\sigma_{yy}$ stresses) the phase diagram of the (1$q$) $\sigma_{xx}$ stress-induced phase. We deduce also in this case the presence of the 1$q$ phase at zero stress over a ~0.1 K temperature interval. We note that within

(*) We also report some values of the $T_{c}$ and $T_{h}$ main $\alpha \rightarrow$ INC transition temperatures which show a decrease of the width of the main hysteresis cycle with increasing $\sigma_{yy}$ stress.
4. Discussion.

Although the dilatometric and birefringence variations are roughly similar, the details which additionally appear in birefringence curves can be explained by the fact that stress and temperature inhomogeneities are much smaller in the path of the light beam than in the whole sample height involved in the dilatation measurements:

- concerning the $1q \to 3q$ transition one can say that the discontinuities observed clearly at medium stress ($\sim 1/60$ of the main $\alpha \to \text{INC}$ transition discontinuity) together with hysteresis are in favor of a 1st order transition in agreement with theory [8]. We also find that the discontinuity increases (with a broadening probably due to stress inhomogeneity) with applied $\sigma_{yy}$ stress. This could explain why it is difficult to observe it at low stress on birefringence curves and was not detected in a preceding paper [6]. On the other hand the depolarization peak becomes very narrow and the shape of the anomalies depends on the exact experimental conditions which could explain why we did not observe it previously [12]. A first-order transition explains the anomalies in light polarization and rotation as being due to the passage of the front phase which induces a gradient stress from volume discontinuity;

- concerning the apparent differences in the shape of the anomalies induced by $\sigma_{yy}$ or $\sigma_{xx}$, this could be due to the narrower range of existence of the $1q$ phase in the latter case and also probably to the difference in the nature of the $1q$ states (in particular the possible existence of domains walls for compressive $\sigma_{xx}$ stresses separating the $1q$ regions (cf. Fig. 1d));

- concerning the $1q \leftrightarrow \beta$ phase transition it is much more difficult reach a conclusion regarding the order of this transition: the very small thermal hysteresis is only observed at middle $\sigma_{yy}$ stresses and, furthermore, the very small discontinuity in birefringence also disappears at higher stresses. The peaks of light depolarization and rotation always
remain up to zero stress. However the possibility of a 2nd-order phase transition cannot be ruled out, since a step-like discontinuity of elastic constant also exists in this case and can lead to non-uniform sample properties along the light path;

— a larger range of existence of the $1q$ phase with $\sigma_{yy}$ than with $\sigma_{xx}$ is in qualitative agreement with theory [8] which however does not predict a $1q$ phase at zero stress. As already emphasized [8] « the role of critical fluctuations and quenched defects could be relevant in this case ». Likewise the role of defects could explain the non linearity at low $\sigma_{yy}$ or $\sigma_{xx}$ stresses (the $3 \times 1q$ (Fig. 1b) phase could exist even at small stress as recently observed by X-ray scattering [17]).

5. Conclusion.

We have shown how the $1q$ phase (previously identified by neutron measurements (under $\sigma_{yy}$ stress) is also obvious from dilatation curves and optical measurements. The $1q$ phase between the $3q$ and $\beta$ phases is marked:

— on dilatation and birefringence curves by two changes of slope (one already known at $1q \leftrightarrow \beta$ and a new one at $1q \leftrightarrow 3q$) separated by a straight line;

— on birefringence ($\Delta \phi$) curves: the straight line is limited by a small (increasing with $\sigma_{yy}$ stress) discontinuity at $1q \leftrightarrow 3q$ and sometimes, with $\sigma_{yy}$, a very small discontinuity at the $1q \leftrightarrow \beta$ transition;

— in light polarisation and rotation along the $Z$ axis by two anomalies (often peaks) at $1q \leftrightarrow 3q$ and $1q \leftrightarrow \beta$ transitions.

We have been able to determine more accurately the phase diagram with $\sigma_{yy}$ stress and to give the phase diagram for the $\sigma_{xx}$ case for the first time. In both cases, the existence of the $1q$ phase at zero stress is clearly established (similar conclusions have been very recently reached from neutron diffraction [18] and elastic light scattering [19]). We are in qualitative agreement with the Landau theory [8] concerning the relative (larger) variation of the temperature existence interval of the $1q$ phase under $\sigma_{yy}$ and $\sigma_{xx}$ stress and the order (1st) of the $1q \leftrightarrow 3q$ transition. However this theory does not lead to a $1q$ phase at zero stress.

Acknowledgments.

The author is grateful to G. Dolino and J. Laizerowicz for suggestions. He thanks M. Vallade for helpful and stimulating theoretical discussions.

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